

ADVANCES IN THE ACTIVATION OF CARBON ELECTRODES FOR OXYGEN REDUCTION

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Oxygen reduction in gas diffusion electrodes attracts considerable interest primarily because of its impact on various energy-related fields, such as fuel cells and metal-air batteries. As an electrocatalyst for this reaction, platinum has traditionally been employed but, due to its high cost, less expensive potential alternatives are being actively searched for. Among these, carbon-supported metal macrocycles exhibit very good activity and stability and are currently employed in mechanically recharged metal-air batteries for electrical traction [1].

In pyrolyzed metal macrocycles the molecular structure of the catalyst is destroyed during the heat treatment so that the metal complex is in fact only a precursor of the actual active material. It is thus appealing to try to reproduce these electrocatalysts starting with different precursors of lower cost and easier availability, and to disclose the reasons for their activity so as to be able to improve their performance.

Literature data show that spinel oxides prove to be active electrocatalysts for oxygen reduction. Since these oxides are obtained by pyrolysis, as a first approach we have investigated the effect of the nature of the precursor on the activity of Co₃O₄-based electrocatalysts.

Co₃O₄ samples were prepared by thermal decomposition at 400 °C of such different precursors as Co nitrate, carbonate, oxalate and citrate both as powders and as thin layers on a suitably pre-treated Ni support. Powders were characterized by XRD, TEM and BET to determine their crystal structure, morphology, particle size and surface area. Oxide powders were then intimately mixed with high surface area carbon and the mixture attached to a Ni support by means of a Nafion[®] binder. Both kinds of electrodes were tested electrochemically by means of cyclic voltammetry in N₂ as well as O₂ saturated KOH solutions, and by steady-state polarization curves for O₂ reduction.

Gas diffusion electrodes were also prepared using the same materials for tests in a pilot plant under galvanostatic conditions in air at 30 mA cm⁻² (geometric). The state of these electrodes were monitored as a function of time by periodically recording polarization curves in situ.

Experimental data showed that Co₃O₄ of different morphology is formed depending on the precursor, although in all cases (but from citrate) the pure spinel phase is formed. The most interesting observation is that Co₃O₄ from the carbonate exhibits a considerably lower particle size, a feature discovered in a previous paper by one of us [2], but not yet mentioned in the literature in the field of electrocatalysis.

Data show that Co₃O₄ from carbonate is not only the most active (Fig. 1) but also the most stable (Fig. 2)

electrocatalyst among the materials tested. Nevertheless, electrodes based on a pure oxide phase exhibit an activity approaching but not equalling that of pyrolyzed metal macrocycles.

In the assumption that the macrocycle participates in the composition of the electrocatalyst resulting from pyrolysis, it was decided to thermally treat a mixture of metal precursor, macrocycle and carbon. Preliminary experimental data will be reported showing that the resulting electrocatalyst is appreciably more active than the pyrolyzed metal macrocycle representing the starting reference for activity.

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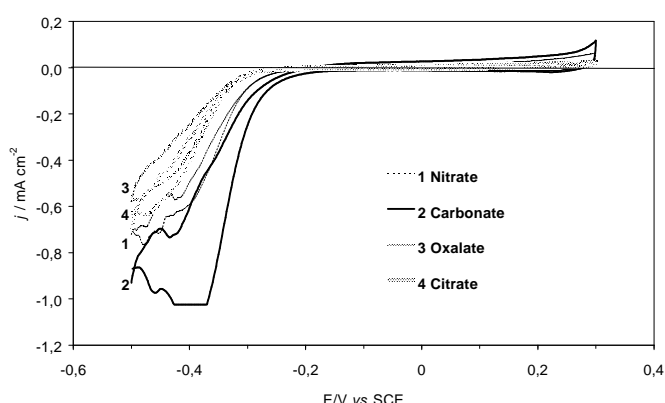


Figure 1 – Voltammetric curves in O₂ saturated solution of Co₃O₄-based electrodes prepared by thermal decomposition of different precursors. 1 mol dm⁻³ KOH; Support: Ni; Active layer: 80 w % carbon + 20 w % oxide.

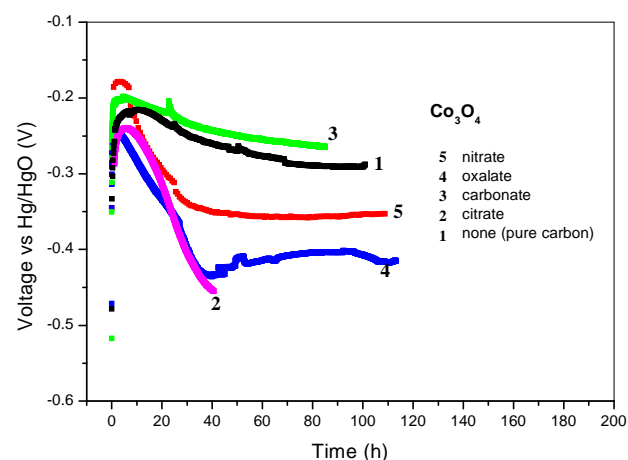


Figure 2 – Long-term performance of gas diffusion electrodes loaded with Co₃O₄ prepared by thermal decomposition of different precursors. 7.5 mol dm⁻³ KOH; 60 °C; 30 mA cm⁻².

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